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Thesis

ATTEMPTS TO PREPARE M - TOLUENE SULPHINIC ACID

FROM

M - TOLUENE MAGNESIUM BROMIDE AND SULPHUR DIOXIDE.

By

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(A.B., Emmanuel College, 1931)

submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1934.

p7932

ACKNOWLEDGEMENTS.

To Dr. J. Philip Mason, I am indebted not only for his generous assistance in the laboratory, but for his kind interest in my work, without which this thesis could not have been written.

I also wish to acknowledge the help which I received from Miss Jane McNeil in translating the original German articles into English.

PURPOSE

It might be interesting here to note that in a bibliography, 1900-1921 of the Grignard reaction, there were catalogued 1552 papers by about 1100 authors. The index contains about 3500 entries of substances to which this reaction has been applied or which have been produced by its aid (1). For all that, the possibilities of this reaction are far from exhausted, and I have endeavoured to prove by this research work another application of this reaction, namely, the preparation of m - toluene sulphinic acid from the Grignard compound and sulphur dioxide, an acid which, to my knowledge, has not yet been produced in this way.

(1) E. Emmet Reid: Introduction to Organic Research p.205 (1924)

TABLE of CONTENTS

		Page
I.	Preface	
	Acknowledgements	1
	Purpose of the Research	2
II.	Table of Contents	3
III.	Introduction	4 - 5
IV.	Resume of Literature	
	Structure of Sulphinic Acids	6 - 7
	Methods of Preparation of Sulphinic Acids	8 - 9
	Methods of Preparation of m - Toluene Sulphinic Acid	10
	Properties of the Sulphinic Acids	11 -12
	Properties of Benzene Sulphinic Acid	12
	Properties of p - Toluene Sulphinic Acid	12
	Properties of m - Toluene Sulphinic Acid	13
	Methods Used in the Manufacture of Sulphinic Acids	14 - 15
	Isolation of Sulphinic Acids	16 - 17
V.	Experimental	
	Outline	18
	Preparation of Reagents	19 - 20
	Diagram	21
	Addition of Sulphur Dioxide	22
	Calculations	23 - 24
	Attempt to Prepare Benzene Sulphinic Acid	25 - 36
	Qualitative and Quantitative Analysis of Phenyl Magnesium Bromide	37 - 40
	Attempt to Prepare p - Toluene Sulphinic Acid	41 - 43
	Qualitative and Quantitative Analysis of p - Toluene Magnesium Bromide	44 - 47
	Summary and Conclusion	48
	Bibliography	49 - 51

Introduction.

In the course of the investigation of the derivatives of sulphurous acid, which was carried out in continuation of the earlier work of Rosenheim & Liebknicht, the alkyl sulphinic acids were studied, especially some unknown derivatives of the latter, in relation to the re-arrangements which they undergo. The yield of sulphinic acid was not satisfactory when prepared by the action of sulphur dioxide on zinc alkyl, or when sulpho-acid chloride was treated with zinc dust. It was expected, therefore, that here as in many other cases, with the help of the Grignard reaction, a convenient method of procedure could be found. Grignard himself, observed the mode of transformation of mono-carboxylic acid by the introduction of carbon dioxide into alkyl magnesium halide.

$$R\ Mg\ X + CO_2 \longrightarrow R\ C(=O)\ O\ -\ Mg\ -\ X$$

This was further studied by Houben and Kesselksulas, as well as by Zelinsky, who supposed that sulphinic acids could be prepared by an analogous use of sulphur dioxide. These expectations were fulfilled without exceptions. The method used was as follows; dry sulphur dioxide was conducted into a volatile solution of an alkyl magnesium halogen conmpound. The gas was absorbed with such great evolution of heat that external cooling of the vessel

was necessary. The compound was then hydrolyzed and acidified with sulphuric acid. The sulphinic acid was obtained. The yield varied between 50% and 60% of the theoretical yield, since products of reduction and rearrangement of the sulphinic acid were readily formed thru the secondary reaction. (1)

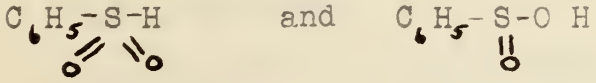
Since all the alkyl halides which form the magnesium alkyl halides by the Grignard Reaction will form sulphinic acids by this reaction (2) it was decided to try to produce m - toluene sulphinic acid from m- toluene magnesium bromide and sulphur dioxide.

However, as m - bromotoluene is an expensive reagent, I endeavoured to perfect my technique by first preparing benzene sulphinic acid, and p - toluene sulphinic acid by the action of sulphur dioxide on benzene magnesium bromide and p - toluene magnesium bromide respectively.

(1) Ber. 37, 2152 (1904) Rosenheim and Singer
(2) " " " " " " "

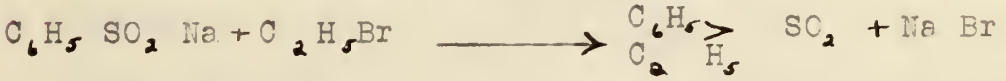
Resumé of Literature.

The amount of literature available on m - toluene sulphinic acid, its preparation and properties is rather sparse. However, much has been written about the sulphinic acids in general. According to Chamberlain (1) sulphinic acids are important because of the phenomenon known as desmotropism which exists in these compounds, the two desmotropic forms being

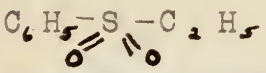


and

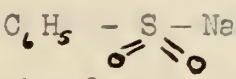
When an alkyl halide reacts with the sodium salt of a sulphinic acid, a sulphone is formed (2)



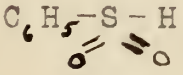
Both radicals are considered as united directly to the sulphur in this compound



Therefore the formula of the sodium salt of benzene sulphinic acid would seem to be



and of the free acid



(1) Joseph S. Chamberlain Organic Chemistry p.524-5(1921
(2) A.F. Holleman, Organic Chemistry p. 74 (1930)

The acid hydrogen is not hydroxyl hydrogen in such a compound, but is linked directly to the sulphur.

The alkaline sulphinates form with chloro- carbonic esters real sulphinic esters (1)

$$C_6H_5SO_2Na + Cl\,CO_2C_2H_5 \longrightarrow C_6H_5S\,O\,O\,C_2H_5 + Na\,Cl + CO_2$$

which are readily hydrolyzed yielding alcohols. Such an ester must be a true ester of sulphinic acid and must be represented by the formula

$$C_6H_5 - SO - OR$$

In all esters of oxygen acids, a radical replaces a hydroxyl hydrogen in the acid, and therefore must be linked to an oxygen. Accordingly, the formula for the ester will be

$$C_6H_5 - SO - OR$$

and the formula of benzene sulphinic acid will be

$$C_6H_5 - \underset{\underset{O}{\|}}{S} - O\,H$$

exactly analogous to that of benzene sulphonic acid.

Thus we have two constitutions for sulphinic acids and their salts, each proven by definite reactions.

(1) Victor Von Richter Organic Chemistry p. 180 (1922)

Methods of Preparation of Sulphinic Acids.

Sulphinic Acids formed by the action of sulphur dioxide on open chain aliphatic or cycloparaffin saturated hydrocarbons in the presence of an anhydride halide of aluminum or bromide, preferably under pressure and at an elevated temperature. (1)

The aromatic sulphinic acids are prepared in a yield of about 80% by the action of sulphur dioxide and aluminum chloride on aromatic hydrocarbons or their halogen derivatives at a low temperature. It is generally necessary to start the reaction with dry hydrochloric acid, but this is not required in the case of phenol ethers. The product is treated with alkali and the sulphinate decomposed by acid. Phenol ethers yield not only sulphinic acids, but also sulphoxides and sulphonium compounds even in the absence of hydrochloric acid (2)

The aromatic sulphinic acids are also obtained (3) by adding to a cold diazo solution a 40% solution of sodium hydrogen sulphite an excess of alcoholic sulphurous acid containing a small quantity of cupric sulphate or another compound of copper. The reaction occurs at 0 - 20° C in the case of aniline, o - toluidine, or methyl anthranilate,

(1) Chem. Abs. 24, 2759 (1931)
(2) Ber. 41, 3215-22 (1908) Emil Knoevenagel and James Kenner
(3) J. Chem. Soc. Abs. 715 (1902) Basler Chemische Dabrik (D.R.P.130,119)

but more stable diazo salts require a higher temperature.

$$2\ R\ N_2Cl + 2\ SO_2 + 2\ Cu \longrightarrow 2\ R\ SO_2\ H + 2\ N_2 + Cu\ Cl_2$$

Schiller and Otto prepared the sulphinic acids by adding zinc dust to a cold alcoholic solution of aryl sulphonyl chloride. The zinc salt was washed with water and decomposed by sodium carbonate. The solution after having been concentrated, was treated with hydrochloric acid in the cold, and the aromatic sulphinic acid was precipitated. (1)

The sulphinic acids are also prepared

(I) by the action of sulphones with sodium (2)

(II) by the action of potassium cyanide or sodium arsenate upon benzol thio - sulphonates (3)

(III) by the decomposition of benzol - sulphydroxamic acid (4)

IV. by the action of sulphur dioxide or sulphur trioxide on zinc alkyls (5)

V. by the action of sulphonyl chloride on the Grignard Compound. (6) and (7)

(1) Ber. 26, 2813 (1893) Schiller and Otto
(2) Victor Von Richter, Organic Chemistry p.180 (1922)
(3) Ber. 41, 3351 (1908) Emil Knoevenagel and James Kenner
(4) Victor Von Richter Organic Chemistry p.180 (1922)
(5) A. 102, 72
(6) Atti real Accad. 14 (1) 169 (1905)
(7) Gaz. Chim. Ital. 35 (2) 136 (1905)

Method of Preparation of m - toluene Sulphinic Acid.

F. H. Müller and F. Wiesinger prepared m - toluene sulphinic acid by the action of sulphurous acid on the m - toluene diazonium acid sulphate (1)

It was also prepared by Gattermann. He diazotized m - toluidine in a dilute solution in the presence of a large excess of acid, saturated the solution with sulphur dioxide at 0°C, and added copper powder in the cold.(2)

(1) Ber. 12, 1348 (1879) F. H. Müller and F. Wiesinger
(2) Ber 32, 1136 (1889) L. Gattermann

Properties of Sulphinic Acids.

General Properties.

The sulphinic acids are

I. Readily oxidized to sulphonic acids (1) and (2)

II. Reduced to mercaptans by zinc and dilute sulphurous acid (3)

III. The alkyl ethers of sulphinic acids R SO O R′ are formed by passing hydrochloric acid into a solution of the acid in the corresponding alcohol, and also by the action of chloro-carbonic ethers Cl CO_2R upon the sodium sulphinate X S O O Na in cold alcohol, C O_2 being evolved. (4)

IV. Isomeric sulphones X S O_2R are formed by the action of alkyl halides upon the sulphinates.(5)

V. The aromatic sulphinic acids yield potassium sulphite and hydrocarbons when fused with potash, (6)

(1) E. de Barry Barnett Preparation of Organic Compounds p.235 (1920)
(2) Watts: Dictionary of Chemistry p.587 (1894)
(3) E. de Barry Barnett Preparation of Organic Compounds p. (1920)
(4) Watts Dictionary of Chemistry p.587 (1894)
(5) Ber. 18 2493 (1885) R. Otto and A. Rossing
(6) Ber. 19 1224 (1886) R. Otto and A. Rossing

VI. The aromatic sulphinic esters are readily oxidized by potassium permanganate and acetic acid to sulphonic esters (1)

VII. The hydroxamic acids of sulphinic acids do not undergo re-arrangement to form thionylamines, as the corresponding carboxylic acids do, but form the corresponding sulphonamides, even when the reactions are carried out in absolute ether at a low temperature. (2)

Benzene sulphinic acid (3) and (4)

Long prismatic crystals, melting point 83° and 84°C.

Decomposes at 100°C.

Slightly soluble in cold water

Very soluble in hot water, alcohol and ether.

P - toluene sulphinic acid (5)

Plates; melting point 85°C

Slightly soluble in cold water

Very soluble in hot water, alcohol and ether.

(1) Ber. 19, 1224 (1886) R. Otto and R. Rossing
(2) J. Am. Chem. Soc. 47, 1353 -7, (1925) H. F. Whalen and L. W. Jones.
(3) Van Nostrand Chemical Annual p.314-15 (1926)
(4) Watts Dictionary of Chemistry p.456 (1886)
(5) J. Chemical Soc. A (1) 336 (1905) Tröger and Hille

M - toluene sulphinic acid

Unstable oil

Slightly soluble in cold ether (1)

(1) J. Chem. Soc. A (1), 336 (1905) Tröger and Hille

Method Used in the Manufacture of Sulphinic Acids.

Sulphinic Acids are manufactured by the action of sulphurous acids and copper powder on the sulphuric acid diazo derivatives of primary aromatic amines (1)

$$C_6H_5N_2O\,SO_2\,C\,H + H_2SO_3 \longrightarrow C_6H_5N_2\,SO_3\,H + H_2SO_4$$

$$C_6H_5N_2\,SO_3\,H + \begin{pmatrix} H_2SO_3 \\ \text{or} \\ Cu \end{pmatrix} \longrightarrow C_6H_5\,SO_2\,H + \begin{pmatrix} H_2SO_4 \\ \text{or} \\ Cu\,O \end{pmatrix} + N_2$$

An improvement of this method is recorded (2) in the British Patent, 12, 871 of 1900. It was found that if the primary aromatic amine is diazotized in a solution of hydrochloric acid instead of sulphuric acid, and then to the diazo-chloride is added sulphurous acid, alcohol and a little copper sulphate, the formation of sulphinic acid occurs more quickly and completely.

This method was again revised by Charles Dreyfus, Ph.D. (3) He diazotized the primary aromatic amine, saturated the diazotized amine with sulphur dioxide, and stirred into the solution finely divided moist cuprous sulphide. The amino group (NH_2) in the aromatic amine is replaced by the sulphinic acid group (SO_2H) during the evolution of nitrogen.

(1) British Patent 26, 179 (1896)
(2) " " 12,871 (1900)
(3) " " 7,283 (1906)

Charles Dreyfus (1) later offered a further improvement of this method of manufacturing aromatic sulphinic acids. After the diazotization of the primary amido compound and the saturation with sulphur dioxide (at a low temperature) a copper compound soluble in the liquid is added, following which is added a reducing agent other than ethyl alcohol. Nitrogen is evolved and the sulphinic acid is produced.

(1) British Patent 13, 054 (1906)

Isolation of the Sulphinic Acids.

According to John Thomas (1) all the sulphinic acids prepared, are precipitated quantitatively as ferric salts from strongly acid solutions on the addition of ferric chloride. The ferric salts form orange coloured precipitates which are filtered and washed and are quite stable in dry air. The sulphinic acids as a class are characterized by this property of yielding orange yellow ferric salts which are insoluble in water and fairly strong mineral acids. The ferric salts are decomposed by alkalis, giving ferric hydroxide and a solution of alkali sulphinate, from which the free sulphinic acid can be precipitated by the addition of hydrochloric acid.

This method of isolating the sulphinic acids as ferric salts has been recorded (2) as being very advantageous for technical purposes, because although the free sulphinic acids or their soluble salts readily undergo oxidation on contact with atmospheric oxygen, the insoluble ferric salts are stable in the air at ordinary temperatures, and the sulphinic acids can be stored or preserved for any period in the more stable form of their ferric salts.

(1) J. Chem. Soc. 95, 342 (1909
(2) British Patent 13, 055 (1906)

However, this process of extraction is not very direct, so I attempted in my work to extract the sulphinic acid from the ether solution with alkali, as the sodium salt, and to precipitate the free acid by a mineral acid. Otto observed that the salts of sulphinic acids might be precipitated from their aqueous solutions by the addition of strong caustics (1) and it seems logical to suppose that the salts of the acids may be extracted from their ether solutions by the addition of strong caustics.

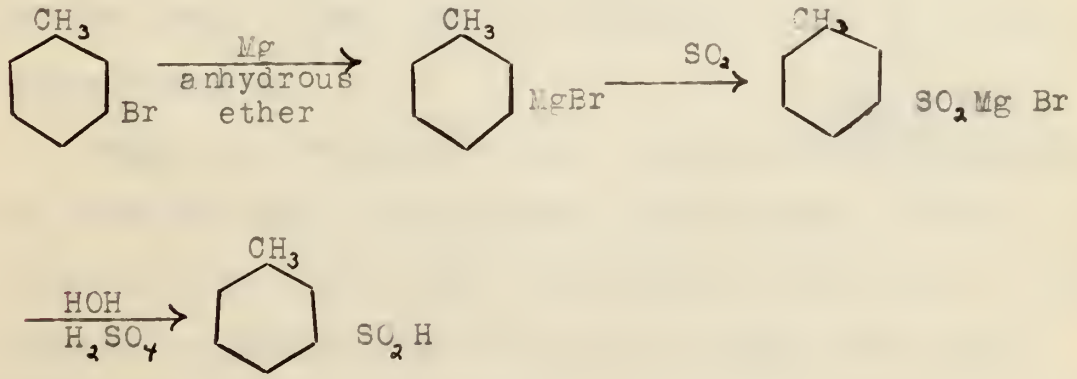
(1) Ber. 26, 1314 (1895) R.Otto

EXPERIMENTAL

Outline

The general method of procedure that will be used in the preparation of m - toluene sulphinic acids, and similar aromatic sulphinic acids from the Grignard Reagent and sulphur dioxide will be as follows: The Grignard Reagent will be prepared from a calculated amount of magnesium turnings , aryl halide and anhydrous ether. The reagent will then be saturated with sulphur dioxide at a low temperature (about $0^{\circ}C$) and the product will be hydrolyzed with water and a mineral acid, after which the sulphinic acid will be extracted from the ether solution.

The chief reactions which will take place in the synthesis of m - toluene sulphinic acid, may be represented by the following equations;



Preparation of Reagents.

Purification of Bromo-benzene.

The bromobenzene was purified by washing it with 10% sodium hydroxide, water, dilute hydrochloric acid and water successively. It was dried over calcium chloride and distilled. The pure product distilled over at 156°C.

Drying the Ether.

The ether was allowed to stand over calcium chloride for several hours, and was then treated with metallic sodium and distilled over sodium. The ether distilled over at 34.5° C.

Preparation of p-bromo toluene.

21 gm. of crystallized copper sulphate, 66 gm. of copper turnings, 51.3 gm. of sodium bromide, 10 gm. of concentrated sulphuric acid and 333 cc of water were refluxed over a flame for 1 - 1½ hours, until the color became yellowish.

When the hydrobromic acid - cuprous bromide solution was ready for use, the diazonium solution was prepared. A solution of 35.6 gm. of p - toluidine and 65.3 gm. of concentrated sulphuric acid in 333 cc of water was cooled below 20°C and diazotized with a solution of 223.3 gm. of sodium in 41.6 cc of water. This required about 7 - 10

minutes with the temperature maintained between 15°- 20° by means of an ice bath.

A round bottom flask was arran ed, containing the hydro-bromic acid-cuprous bromide solution for steam distillation. After the copper sulphate was heated to boiling, the diazonium solution was added gradually thru a separatory funnel, passing a vigorous current of steam thru the reaction mixture at the same time. The procedure required about one hour.

The aqueous distillate was made alkaline with sodium hydroxide solution and the p - bromotoluene was separated from the water layer. The crude product weighed about 40 gms. This was washed with concentrated sulphuric acid and water, dried over calcium chloride, filtered and distilled. The yield was about 35 gms. (1)

$$P - C_6H_4CH_3NH_2 + H_2SO_4 + HNO_2 \longrightarrow P\cdot CH_3C_6H_4N_2OSO_3H + 2\,HOH$$

$$p - CH_3C_6H_4N_2OSO_3H + HBr\ (CuBr) \longrightarrow p\text{-}CH_3C_6H_4Br + N_2 + H_2SO_4$$

This process was repeated, and the yield was again about 35 gms.

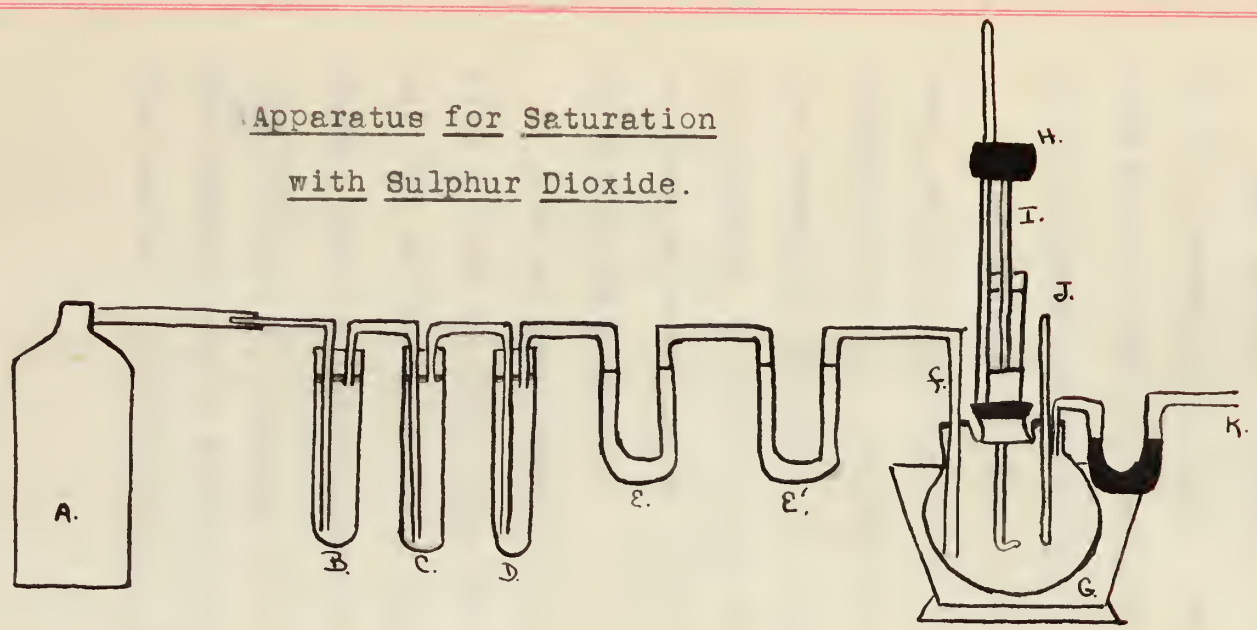
Preparation of Sulphur Dioxide.

Some of the sulphur dioxide used in the experimental work was generated by letting sulphuric acid fall drop by drop from a separatory funnel onto solid sodium bisulphite. The gas was dried by sending it through the drying apparatus pictured in the diagram.

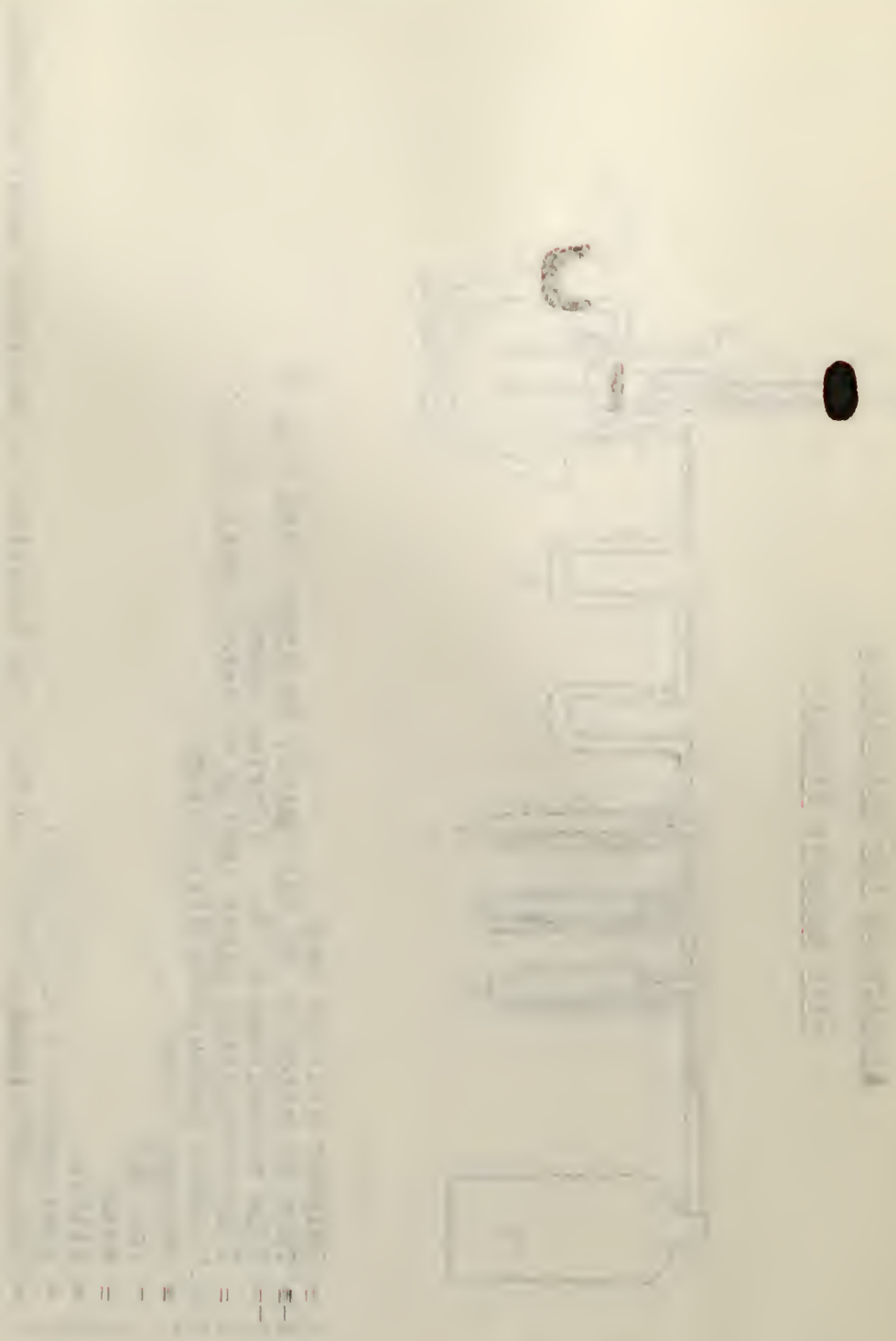
$$NaHSO_3 + H_2SO_4 \longrightarrow SO_2 + NaHSO_4 + H_2O$$

(1) J.B.Cohen Practial Organic Chemistry

Apparatus for Saturation with Sulphur Dioxide.



A = Sulphur dioxide tank
B = Tube to catch H_2SO_4 that might be drawn back from C
C = Tube containing H_2SO_4 (drying agent)
D = Tube containing glass tubing to catch spray from C
E-E'. U tubes containing dessichlora
F = entrance tube
G = ice bath
H = motor
I = stirrer
J = thermometer (-10° - 100°)
K = tube contaiming mercury so that the solution is saturated under pressure.



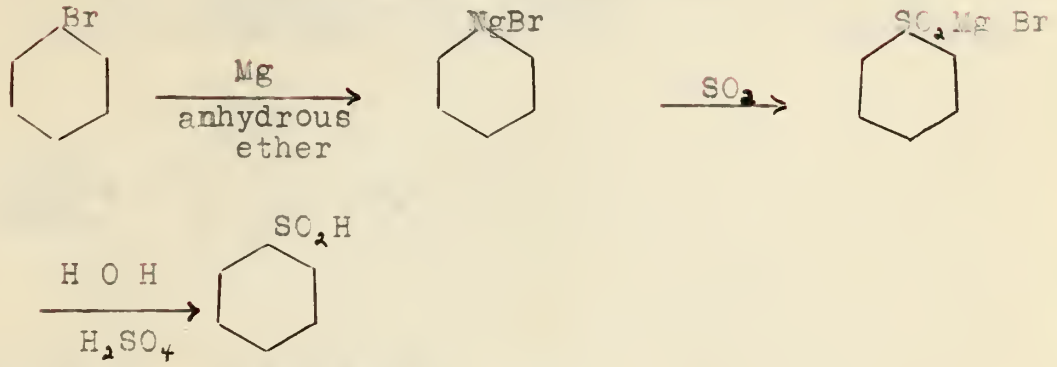
Addition of Sulphur Dioxide.

The sulphur dioxide is added from the apparatus shown in the preceding diagram. The success of the experiment depends in part upon the absolute dryness of the gas. This drying apparatus has proved to be expedient.

The purpose of the U tube arranged in the further neck of the flask is to indicate complete saturation with sulphur dioxide. The tube is filled with mercury and when the re-action mixture is becoming saturated with the gas, the mercury is forced from the tube. Of course this method is only succesful when the rest of the apparatus is positively without any leaks.

The ice-bath picture in the diagram is another essential factor in this experiment. The Grignard compound must be cooled below $0^{o}C$, before the sulphur dioxide is added, and the temperature must be kept around $0^{o}C$ during the addition of the gas, in order to prevent decomposition. The temperature is successfully regulated by the use of the ice bath and further controlled by the rate of stirring.

Calculations



Molecular weight of C_6H_5Br = 156.9

" " " Mg = 24.32

" " " H_2SO_4 = 98

" " " $C_6H_4C\,H_3Br$ = 170.92

Using 50 gm. C_6H_5Br

50 : 156.9 :: X : 24.32

X = 7.7 gm. Mg.

50 : 156.9 :: X : 49

X = 15.6 gm. H_2SO_4

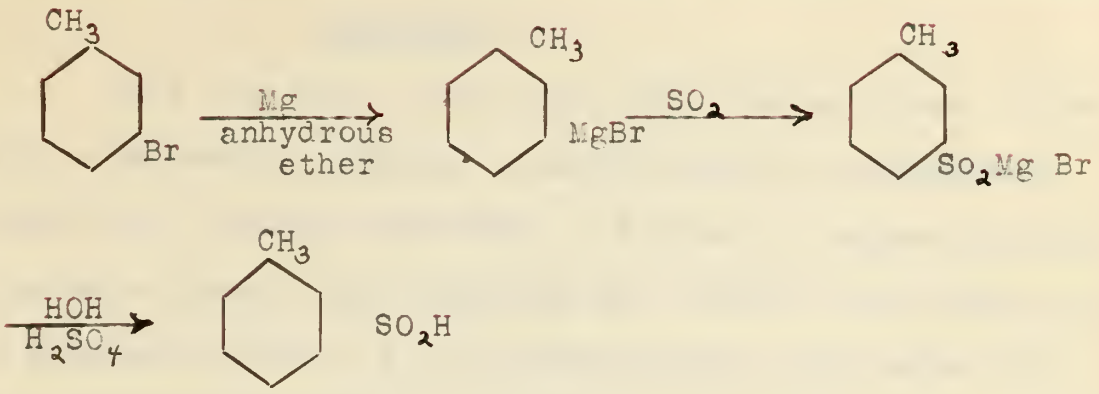
Using 20 gm. C_6H_5Br

20 : 156.9 :: X : 24.32

X = 3.1 gm. Mg.

20 : 156.9 :: X : 49

X = 6.2 gm. H_2SO_4



Using 20 gm. $C_6H_4CH_3Br$

20 : 170.92 :: X : 24.32.

X = 2.84 gm. Mg.

20 : 170.92 :: X : 49

X = 5.7 gm. H_2SO_4

PROCEDURE.

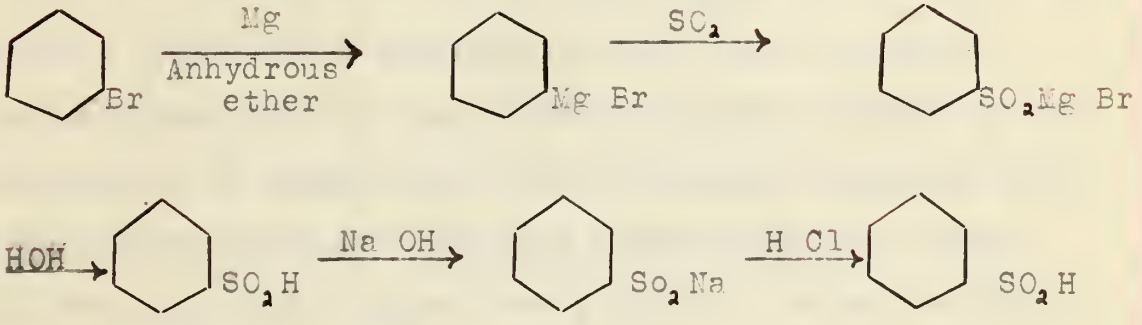
In a one-liter three-neck round bottom flask, fitted with a mechanical stirrer, a mercury seal, a separatory funnel and a reflux condenser, 7.7 grams of magnesium turnings were placed. The magnesium was covered with about 45 cc of anhydrous ether. 5 cc of bromobenzene were added and the stirring was begun. As the reaction did not start, a crystal of iodine was added and the flask was gently warmed by dipping it into a pan of hot water. When the reaction had started, the hot water was removed and a solution of 29 cc of bromobenzene in 250 cc of anhydrous ether was dropped onto the magnesium during the course of two and one-half hours. The rate of dropping was regulated so that the ether refluxed gently all the time. The stirring was continued for about fifteen minutes after the reaction was completed, and then the excess magnesium was filtered off.

The mixture was surrounded with an ice and salt bath, and the separatory funnel was replaced with a two-hole rubber stopper containing a thermometer (bulb immersed in the reaction mixture) and a glass tube, the outer end of which was connected to a mercury trap. The trap was used to produce pressure. A glass tube extended from the mercury trap to a wash bottle, where the excess of sulphur dioxide was absorbed.

When the temperature of the reaction mixture had fallen below 0°C, the condenser was replaced by a tube 10 mm. in diameter and adjusted so that the end of the tube was 50 mm. above the surface of the reaction mixture. The reaction mixture was stirred and sulphur dioxide was added thru the tube from a cylinder after passing thru the drying apparatus (shown in the diagram). The sulphur dioxide was added as rapidly as it was used up. The temperature did not rise above 8°C, controlled by the rate of stirring. The addition of sulphur dioxide was continued for three hours, at which time the temperature fell to -5°C and the reaction was completed.

The flow of sulphur dioxide was shut off, and the two- hole rubber stopped was replaced with a dropping funnel. 12.4 gm. of sulphuric acid and about 100 cc of water were added drop by drop, thru the funnel, with continuous stirring. Hydrolysis was effected and two layers were formed. The two layers were separated and an attempt was made to extract the acid from the ether layer with 10% sodium hydroxide, as the sodium salt of the acid. The sodium salt solution was acidified with dilute hydrochloric acid, and evaporated to one-half its volume. The result was negative.

The following reactions would be expected to take place in the above synthesis:



The synthesis was repeated with 20 gm. of bromobenzene, 3.1 gm. of magnesium turnings and 110 cc of anhydrous ether. A quantitative analysis was made of the compound by which it was determined that most of the magnesium used was reacting to form phenyl magnesium bromide. As a complete quantitative and qualitative analysis of the Grignard Compound is given later in this thesis, and as the exact amount of magnesium used was not accurately determined, the figures from this analysis are not recorded here.

The Grignard Compound was made up, starting with 20 gms. of bromo-benzene and the calculated amount of magnesium turnings and anhydrous ether. The solution was allowed to stand for two days during which time colorless crystals settled out. There was a possibility that these crystals might be phenol, for if there was any phenol present in the bromobenzene, it would react with the phenyl magnesium bromide to form benzene and magnesium bromo-phenolate, which would react in turn to give free phenol. A water solution of the crystals was tested with ferric chloride, but the characteristic color did not appear. This showed that the crystals were not phenol.

It was impossible to take a melting point of the crystals, for they were very deliquescent. They were insoluble in ether, and became white when desiccated.

A few of the crystals were dissolved in water with the formation of a white precipitate, which disappeared on the addition of hydrochloric acid.

10% sodium hydroxide was added to a water solution of the crystals. A gelatinous precipitate was formed. These tests identify magnesium as being present in the compound.

The presence of bromine was established by the silver nitrate test. Therefore it was concluded that the crystals were magnesium bromide-etherate.

The above synthesis was repeated with 20 gms. of bromobenzene, 3.1 gms, of magnesium turnings and 118 cc. of anhydrous ether. 6.2 gms. of sulphuric acid were used in the hydrolysis of the reaction mixture. An attempt was made to extract the acid as the sodium salt with a 10% solution of sodium hydroxide and to precipitate the free acid with hydrochloric acid. A small amount of oil resulted.

The process was again repeated, using the same quantities as in the last run. After the compound was saturated with sulphur dioxide and hydrolyzed, the two layers were separated and the ether layer was evaporated on a water-bath, heated to 45°C. After the ether was driven off a charred oily substance remained.

An attempt was made to extract any acid that might have been present in the water layer as the ferric salt (1) with concentrated ferric chloride solution. The ferric salt of the acid was expected to separate out as a bright orange yellow precipitate, but the precipitation did not occur. There evidently was no sulphinic acid present in the water layer.

The synthesis was carried out in the same manner as above, starting with 20 gms. of bromo-benzene and the calculated amount of magnesium turnings and ether. The sulphur dioxide which was used, was generated as described in the chapter entitled "Preparation of Reagents".

(1) J. Chem.Soc. 95, 342 (1909) John Thomas

After the compound was hydrolyzed, the two layers were separated, and the ether was placed in a round-bottom flask. A one-hole stopper was placed in the neck of the flask, fitted with a piece of glass tubing which was joined with a piece of rubber tubing. The rubber tubing was connected to the suction pump and the excess sulphur dioxide was drawn off. This precaution was taken to eliminate the possibility that much of the alkali would be used up in reacting with the excess gas. The ether layer was allowed to evaporate spontaneously, but a dark oily substance resulted.

Another run was made, starting with one half the above quantities of bromo-benzene, magnesium turnings and ether, to be used as check on the saturation with sulphur dioxide. After the temperature had fallen below $0^{o}C$, an upright tube was placed in the further neck of the flask and the stream of gas was turned on. After the air had been expelled, the upright tube was replaced with a U tube filled with mercury as shown in the diagram. After an hour and fifty minutes the temperature of the reaction mixture had fallen below $0^{o}C$ and the mercury was gradually forced from the U tube by the pressure exerted by the excess sulphur dioxide. This proved that the gas was

being absorbed by the Grignard Compound.

According to Rosenheim and Singer (1) the magnesium salt of benzene sulphinic acid should have separated. out at this point in a white crystalline mass. This separation did not occur. The ethereal solution had turned a reddish brown during the process of saturation and this led me to believe that the compound $C_6H_5SO_2Mg$ Br had formed (the bromine lending the color to the solution) instead of the compound $(C_6H_5SO_2)_2Mg$ as was expected according to predictions.

The compound was hydrolyzed and the two layers were separated. The ether layer was allowed to evaporate spontaneously. An oil resulted which had the odor of phenol. A drop of bromine water was added to a few drops of the oil. The bromine water was decolorized. Two more drops of bromine water were added to the solution, and a white precipitate formed. This is a test for phenol. The precipitate was filtered and dried and a melting point was taken.

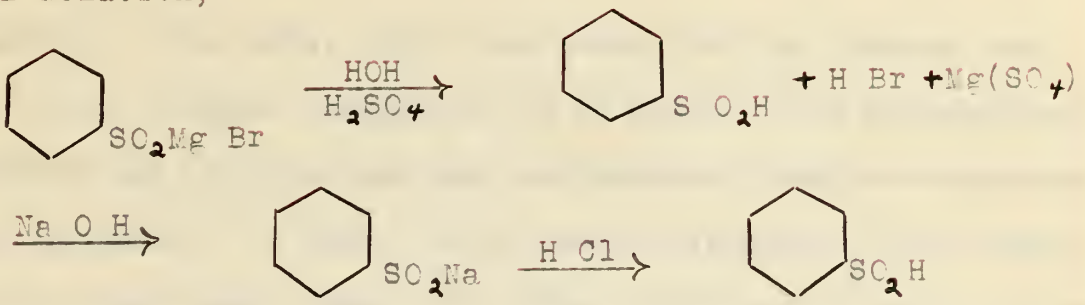
Melting Point = 93°C.

" " of tri-bromo phenol = 96°C .

The precipitate was tri-bromo phenol and the oil was phenol. It was expected that the following reactions would have taken place if $C_6H_5SO_2Mg$ Br had formed in the ether-

(1) Ber. 37, 2152 (1904) Rosenheim and Singer

eal solution,



The water layer was extracted with ether, and the ether was allowed to evaporate spontaneously. No residue.

The Grignard compound was prepared with 20 gms. of bromobenzene and the calculated amounts of magnesium turnings and ether. The compound was saturated with sulphur dioxide, using the apparatus described above to indicate complete saturation. After the saturation was completed, the flask was removed from the ice-bath and the mixture was refluxed for a few minutes before hydrolysis was effected. An attempt was made to extract the acid again as the sodium salt with sodium hydroxide, and to precipitate the free acid with hydrochloric acid, but an oil separated out.

The synthesis was repeated with the above amounts of reagents; the compound was saturated with sulphur dioxide and hydrolyzed in the cold. The same method of extraction used directly above, was employed. A cloudiness resulted which did not precipitate out or increase on

standing. The water layer was evaporated to dryness and the solid residue was ground up in ether. The undissolved portion was filtered off and the ether allowed to evaporate spontaneously. A small white residue remained after evaporation had taken place, but this proved to be sodium chloride which evidently dissolved in the water present in the ether.

Phenyl magnesium bromide was prepared and the ethereal solution was saturated with sulphur dioxide in the cold. Hydrolysis was effected, and the ether layer was extracted with sodium hydroxide. The alkaline solution was acidified with hydrochloric acid and the solution was extracted with ether. The ether solution was placed in an evaporating dish and allowed to evaporate spontaneously. Colorless needle-like crystals settled out in a dark charred solution upon standing over night. The evaporating dish was tipped so that the crystals were out of contact with the liquid, with the expectation that more crystals would separate out. It was allowed to stand for a few more hours. The crystals disappeared; evidently due to the fact that they were highly volatile.

The original ether layer (which had already been extracted with sodium hydroxide) was placed in an evaporating dish and allowed to evaporate spontaneously. The residue

was dissolved in an aqueous solution of sodium hydroxide, and filtered. The residue was washed with dilute acid and water, and dried. The melting point was taken.

Melting point = 64°C

" " of diphenyl 69°C

The residue was diphenyl formed as a biproduct during the reaction. The alkaline filtrate was acidified in order to precipitate any sulphinic acid that might be present. No acid separated out.

The synthesis was repeated, but after charging the ethereal solution with sulphur dioxide in the cold, about 5 cc of the solution was placed in a large test tube and the ether was evaporated off. A solid compound remained. The compound was dissolved in water. A white precipitate of magnesium hydroxide settled out of the solution. Hydrochloric acid was added (substituted here for sulphuric acid, for it might make the subsequent purification of the product easier, due to its greater volatility.) Magnesium chloride formed and a pale yellow oil. The oil was extracted with ether, and the ether was allowed to evaporate spontaneously. An oil resulted.

The ether was evaporated off another portion of the ethereal solution. The oil which formed was extracted with ether, and an attempt was made to extract the acid

from the ether layer with sodium hydroxide. The two layers were separated and the alkaline portion was acidified. Cloudiness resulted.

The process used above was repeated, but after the attempted extraction as the sodium salt and the subsequent acidification with hydrochloric acid, an attempt was made to extract the acid with ether. The two layers which had formed were separated, and the ether layer was allowed to evaporate spontaneously, but an oil was the result.

The ether was driven off a fourth portion of the reaction mixture. The compound was hydrolyzed and acidified with hydrochloric acid. Concentrated ferric chloride was added to the acid solution (1) but the acid was not precipitated in the form of the ferric salt as was expected.

The ether was evaporated off another portion of the solution and hydrolysis was effected. A Yellow oil was the result. The liquid was decanted and Smile's Test for sulphinic acids was applied to the oil. (2) The acid was dissolved in cold concentrated sulphuric acid and one drop of anisole was added. A blue color should have been produced if any sulphinic acid was present, due to the formation of a para-substituted aromatic sulphoxide by the elimination of water. However, a dark brown color was the

(1) J. Chem. Soc. 95, 342 (1909) John Thomas
(2) H. T. Clarke A Handbook of Organic Analysis. p.48 1920

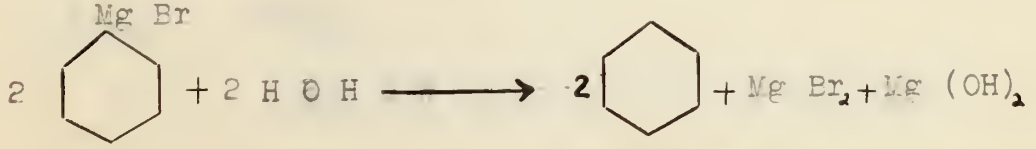
result of this test, which may have indicated that the sulphinic acid was not present, or which may have been caused by the impurities present in the oil.

The solid compound was filtered off, and recrystallized from water. The compound became an oil when it was heated in the water. Part of the water was evaporated off, the beaker was removed from the flame, and the solution was cooled suddenly, the sides of the beaker being rubbed constantly with a glass rod. The compound did not settle out again as a solid, but remained as an oil.

Qualitative and Quantitative Analysis of Grignard Compound.

Since the sulphur dioxide was apparently not adding on to the Grignard Compound, as described in the literature, it was decided to make a qualitative and quantitative analysis of the compound, and to try to isolate the diphenyl, the chief product of the reaction, as well as benzene

The phenyl magnesium bromide was prepared with 20 gms. of bromobenzene, 118 cc of anhydrous ether and 3.1114 gms. of magnesium. 2 cc of the phenyl magnesium bromide was decomposed with water and a titration was made to determine the amount of magnesium which had reacted to form the Grignard Compound.



(1)

$$Mg(OH)_2 + 2\,HCl \longrightarrow MgCl_2 + 2\,HOH$$

2 cc C_6H_5MgBr — Total Volume 105 cc

.1N HCl

15.55 cc
34.50 "
18.95

.0967 N Na_2CO_3

20.6 cc
20.85 cc
.25 "

(1) Ber. 61, 708 (1928) J. Meisenheimer

$\frac{a}{.25} = \frac{.0967}{.1}$

$a = .24175$ cc

18.95 cc
.24 "
18.71 " of acid actually used

36.5 X .1 X .01871 = .0682915 wt.of H Cl

$\frac{X}{24.32} = \frac{.06829}{36.5}$

X = .0456 gm. of Mg in 2 cc of Grignard

= 2.3940 " " " which reacted to form Grignard

2 cc C_6H_5 Mg Br
.1N H Cl
14.38 cc
34.92 "
18.54 "

Total Volume - 105 cc
.0967 Na_2CO_3

36.5 X .1 X .01854 = .067671 weight of H Cl

$\frac{X}{24.32} \quad \frac{.06761}{.36.5}$

X = .0439 gm. of Mg in 2 cc of Grignard

= 2.3047 " " " which reacted to form Grignard

75.5% Percentage of Mg which reacted to form Grignard

The remaining portion of the Grignard Compound (100cc) was decomposed with water, and the magnesium hydroxide was dissolved in hydrochloric acid. The two layers were separated, and the ether was distilled off the ether layer. The residue, a reddish liquid was distilled and the boiling point of the distillate was taken. The boiling point was 79 C, which identified this compound as benzene, the yield of which was 5.5 cc.

Theoretical Yield of Benzene.

.755 X 20 = 15.10 gm. of C_6H_5Br which reacted to form Grignard.

Molecular Weight of bromobenzene = 156

" " " benzene = 78.05

15:10 : 156 :: X : 78.05

x = 7.5 gm. theoretical yield of benzene from total volume

= 7.1 gm. theoretical yield of benzene from 100 cc

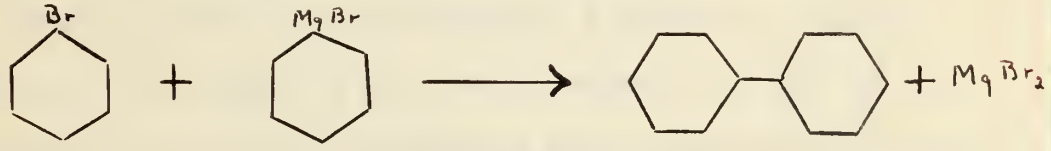
= 8.1 cc

Actual yield of benzene from 100 cc = 5.5 cc

% yield of benzene = 67.97%.

The residue from the distillation was a brownish oily substance. This was allowed to stand for a few days, during

which time crystals settled out. The crystals were weighed and a melting point was taken. The crystals melted at 64°C, which indicated that they were diphenyl formed as a biproduct of the reaction.



Weight of the crystals on watch glass = 27.3457

" " " watch glass = 26.1725

" " " crystals = 1.1733

If all the bromobenzene reacted to form phenyl magnesium bromide and diphenyl, the theoretical yield of diphenyl would be 2.45 gm. However, this is merely an assumption, and a percentage yield calculated on this basis would be of no value.

The diphenyl was recrystallized from alcohol and boneblack and definitely identified by a melting-point determination.

Attempts to prepare p Toluene Sulphinic Acid.

P - Toluene magnesium bromide was prepared by the same method used to prepare phenyl magnesium bromide, starting with 10 gm. of p - bromotoluene, 1.6350 gm. of magnesium and 60 cc of anhydrous ether. The reaction did not run very smoothly as the following calculations will show

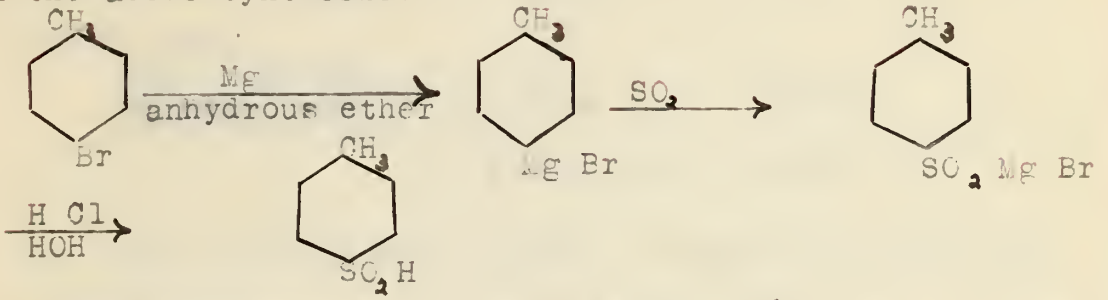
Weight of boat and Mg	=	144.2682 gms.
" " "	=	143.1294 "
" " "	=	1.1388 "

Weight of Mg used	=	1.6350 gms.
" " " remaining	=	1.1388 "
" " " which reacted	=	.4962 "

Percentage of Mg which reacted to form the Grignard Compound.

The compound was charged with sulphur dioxide in the cold and hydrolyzed with a 2.13 gm. of hydrochloric acid and water. The two layers were separated and the ether layer was evaporated. An oil was formed.

The following reactions were expected to take place in the above synthesis.



The syntheses was repeated with 1.5629 gm. of magnesium, 10 gm. of p' - bromotoluene and 60 cc of anhydrous ether.

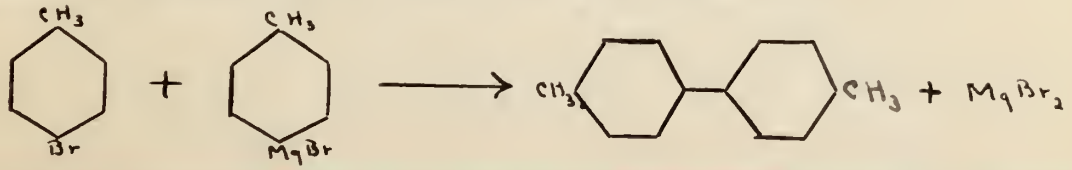
Weight of Mg used = 1.5629 gm.

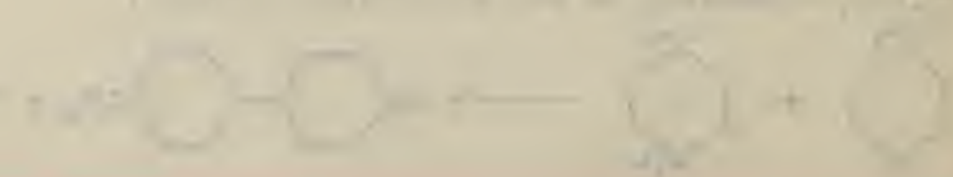
" " " remaining = 1.2888 "
" " " which reacted .2741 "

Percentage of Mg which reacted to form Grignard Compound = 17.5%.

The compound was charged with sulphur dioxide in the cold and hydrolyzed with 2.13 gm. of hydrochloric acid. The two layers were separated and the ether layer was extracted with 10% sodium hydroxide. The alkaline solution was acidified with concentrated hydrochloric acid. A cloudiness appeared in the flask.

The ether layer which was just extracted was allowed to evaporate spontaneously. It was expected that p - p' ditolyl would result., formed as a bi-product of the reaction, according to the following equation;





The residue consisted of needlelike crystals in a brown oil. Filtered the crystals, dried and took the melting point.

Melting point of crystals = 116°C

" " " p-p' ditolyl = 121°C

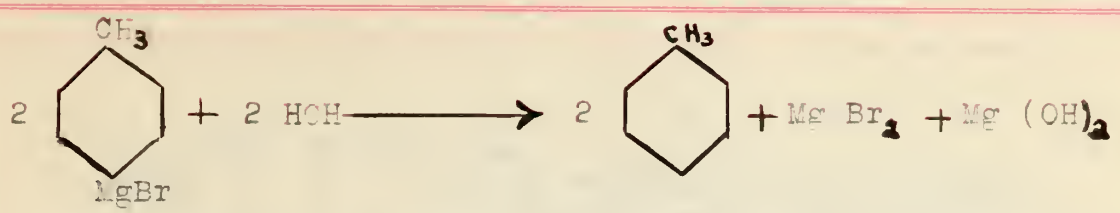
The crystals were ditolyl, formed as a bi-product of the reaction.

Qualitative and Quantitative Analysis of Grignard Compound.

It was decided that since the sulphur dioxide, was not evidently adding on to the ring, to make a qualitative and quantitative analysis of the Grignard Compound. The p - toluene magnesium bromide was made up, starting with 10 gm. of p-bromo toluene, 60 cc of anhydrous ether and 1.5095 gm. of magnesium turnings. It was found, however that only 1.17% of the magnesium had reacted to form the Grignard, so this run was discarded.

The lack of success in this reaction was probably due to impurities in the p - bromotoluene, so more of the reagent was made (as described in the chapter entitled, "Preparation of Reagents") and purified. The p - toluene magnesium bromide was prepared with 10 gm. of p- bromo toleune, 60 cc of anhydrous ether and 1.3978 gm. of magnesium.

2.5 cc of the Grignard Compound was decomposed by water according to the following equations, and a titration was made.



$Mg(OH)_2 + 2\,HCl \longrightarrow MgCl_2 + 2\,HOH$

2.5 cc $C_6H_4CH_3MgBr$ Total Volume 47 cc

.1N H Cl .0967 N Na_2CO_3

11.32 cc
23.60 "

$36.5 \times .1 \times .01228 = .044822$ weight of H Cl

$$\frac{X}{24.32} = \frac{.04482}{36.5}$$

X = .0298 gm. of Mg. in 2.5 cc of Grignard
= .56024 " " " which reacted to form Grignard

2 cc $C_6H_4CH_3MgBr$

.1N H Cl .0967 N Na_2CO_3

23.60 cc 20.2 cc
33.57 " 20.42 "
10.17 " .22

$$\frac{a}{.22} = \frac{.0967}{.1}$$

a = .2127

10.17 cc
.21 "
9.96 " acid actually used

$36.5 \times .1 \times .00996 = .036354$ weight of H Cl

$$\frac{x}{24.32} = \frac{.03635}{36.5}$$

x = .02438 gm. of Mg in 2 cc
= .57293 " " " which reacted to form Grignard

1.3978 gms. of Mg. used
.5666 " " " which reacted to form Grignard
.8312 " " " " did not react to form Grignard
Percentage of Mg. which reacted to form Grignard = 47.68%

The remaining volume of the Grignard Compound (40cc) was decomposed by water, and the magnesium hydroxide was dissolved in hydrochloric acid. Two layers were formed which were separated, and the ether was distilled off the ether layer. The residue, a reddish liquid, was distilled, and the boiling point of the distillate was taken.

Boiling Point = 110°C.

The distillate was toluene.

Theoretical Yield of Toluene

Molecular weight of p -bromotoluene = 170

" " " toluene = 78.05

.4768 X 10 = 4.768 gm. of p - bromo toluene

4.76 : 170 :: X : 78.05

Theoretical yield X = 2.17 gm. of toluene in total volume
= 2.5 cc " " in total vol.
= 2.1 cc " toluene in 40 cc of Grignard.

Actual yield = 1.4 cc
Percentage " = 66.6 %.

The residue was a reddish oily substance, which was allowed to stand in an evaporating dish for a few days, during which time needle-like crystals formed.

Melting point of the crystals = 117°C

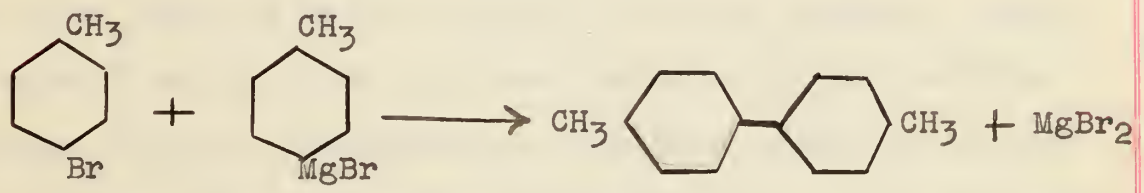
" " of p - p'ditolyl = 121°C

Weight of crystals on watch glass = 26.7290 gm.

Weight of watch glass = 26.1725 gm.

Weight of Crystals = .5565 gm.

The crystals were purified and the melting point was determined. The crystals melted at 120°C and were thus proven to be p - p'ditolyl which was formed as a bi-product of the reaction.



Summary and Conclusion.

(1) A resume of the literature is given, in which the constitution of, the methods of preparation of, and the properties of sulphinic acids, are discussed.

(2) The experimental work is given in full detail.

It was found thru experimentation with phenyl-magnesium bromide and p - toluene magnesium bromide, that the sulphur dioxide was not adding onto the Grignard Compound as described in the literature. Therefore, a qualitative and quantitative analysis of both of these Grignard Compounds was made, and the chief bi-product of each reaction, namely di-phenyl and p - p'ditolyl was isolated, as well as some benzene from the decomposition of phenyl magnesium bromide and toluene from the similar treatment of p - toluene magnesium bromide.

Since the sulphur dioxide did not add onto either of the two Grignard Compounds mentioned above, it was deemed unnecessary to experiment with m - toluene magnesium bromide,for the reaction would be entirely analagous.

There is a possibility for future research on this problem, for it may be that under a different set of temperature and pressure conditions, the sulphur dioxide would add onto the Grignard Compound, and the sulphinic acid would be formed.

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